

Detection of iron in lithium niobate by laser-induced fluorescence of sputtered atoms

Victor M. Bermudez, Jeffrey W. Hudgens, and Mark A. Hoffbauer

U.S. Naval Research Laboratory, Washington, D.C. 20375.

Received 20 July 1983.

One of the most significant materials-related problems in integrated optics (i.e., LiNbO_3) technology is the question of optical damage,¹ which occurs as a result of photoionization of defects and/or metal-ion impurities followed by electron capture at deep traps. The charge separation thus created (which is anisotropic in ferroelectric crystals such as LiNbO_3) changes the indices of refraction of the material via the electrooptic effect. The most important impurity is believed to be Fe^{2+} ; hence, there is a need for a sensitive, yet simple and nondestructive, technique to detect iron in LiNbO_3 based devices after fabrication.

In this Letter, we describe a preliminary formulation of such a method, which is but one specific application of a very general procedure. The technique is based on laser-induced fluorescence (LIF) of species ejected from a sample surface by ion impact. This approach has already been used in numerous studies of laser ablation,² sputtering-yield measurement,³ sputtered-atom velocity distributions (Refs. 4-6 and works cited), molecule-surface scattering,⁷ plasma etching,⁸ and catalysis.⁹ However, this is the first report of the use of this technique for elemental analysis of solids. LIF offers the advantage of detecting neutrals (as well as ions) which are often the dominant species leaving the surface.^{10,11} Also the technique is completely optical; hence, charging of insulating samples presents no difficulties, and there are no special requirements as to the experimental ambient other than those dictated by the method of ejecting material from the surface.

A schematic diagram of the apparatus is shown in Fig. 1. The frequency-doubled output of an excimer-pumped dye laser provided the UV probe beam at 296.69 nm with an energy of ~ 1 mJ/pulse, which was attenuated to ~ 60 μJ /pulse for these experiments. The experimental chamber is a small ($\sim 0.8 \times 0.5 \times 0.5\text{-m}^3$) system constructed from standard 3-way and 6-way crosses with 70-mm (2.75-in.) flanges. The LIF is detected by an end-on phototube (EMI 9924QB) mounted just outside a sapphire window. A pair of lenses inside the chamber collects the fluorescence, and a filter

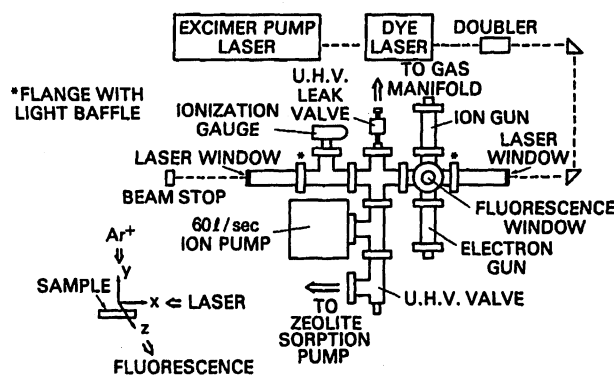


Fig. 1. Schematic diagram of the vacuum system and optical configuration with the dashed line indicating the laser excitation. Inset shows the sampling geometry with the surface under investigation lying in the x - z plane. The sample can be rotated about the z axis. The diagram is not to scale.

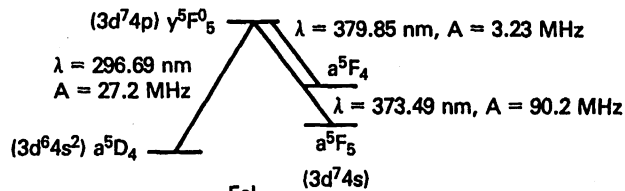


Fig. 2. Part of the zero-valent (Fe I) iron energy level diagram (Ref. 12) showing the excitation and emission processes. The wavelengths λ and transition rates A are given in Ref. 13.

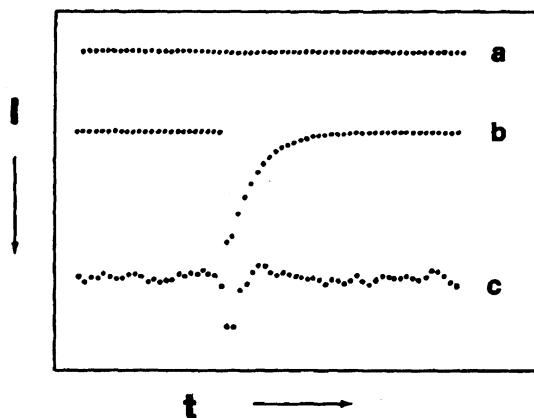


Fig. 3. LIF signals obtained for a Ar^+ beam off (showing scattered light background) and b Ar^+ beam hitting Fe foil (3 keV, $\sim 600 \mu\text{A}/\text{cm}^2$). Trace c is the difference signal (Ar^+ beam on minus Ar^+ beam off) for LiNbO_3 sample at a gain of 512 relative to a and b. The total sweep width is $60 \mu\text{sec}$. The time constant of the signal decay is determined by the electronics.

Table I. Parameters Used to Calculate Fluorescence Yield ^a

Laser power density, $I_L = 95 \text{ kW}/\text{cm}^2$; laser linewidth, $\Delta\lambda_L = 0.005 \text{ nm}$
Laser wavelength, $\lambda_0 = 296.69 \text{ nm}$; laser pulse width, $t_L = 20 \text{ nsec}$
Transition rates: $A_{21}^b = 27.2 \text{ MHz}$; $A_{23}^c = 93.4 \text{ MHz}$; $A_{24}^d = 90.2 \text{ MHz}$
Level 1 degeneracy, $g_1 = 9$; level 2 degeneracy, $g_2 = 9$
Time during which atom is in sampling volume, $t = 1 \mu\text{sec}$
Yield, $Y = 0.87 \text{ photons}/\text{atom}/\text{pulse}$

^a Using theory and notation of Wright *et al.*⁴

^b For excitation transition, $1 \rightarrow 2$.

^c Sum of rates for all sublevels of level 3.

^d Rate for actual fluorescing transition.

^e Assuming sputtered-atom velocity of $10^5 \text{ cm}/\text{sec}$ (Ref. 4) and sampling volume of 1 mm^3 .

combination between the window and the detector attenuates scattered laser light. The filters consist of a 0.5-N solution of SnCl_2 in HCl (10-mm path length), which exhibits a sharp cutoff for $\lambda < 300 \text{ nm}$, together with a visible-absorbing glass filter (Corning 7-54). Avoiding the use of a monochromator permits a very compact and efficient light collection system. The entrance and exit windows incorporate a single light baffle in each mounting flange. In general, when the excitation and fluorescence wavelengths are closer, a much more elaborate set of light baffles will be required. The sample consisted of a stainless steel plate to one side of which was glued (with In metal) pieces of LiNbO_3 and Si. A piece of pure Fe foil was attached to the other side. The LiNbO_3 was a polished Y-cut wafer and the Si a (111)-oriented n -type polished electronic-grade wafer. Both were used as received from the respective suppliers following ultrasonic cleaning in isopropanol. All steel parts of the sample holder were masked with Al foil.

Figure 2 shows the appropriate part of the Fe I (zero-valent iron) energy level diagram.^{12,13} Although there are many other levels lying between the a^5D ground and y^5F^0 excited states, electric dipole radiative decay of y^5F^0 to these states is forbidden by the angular momentum selection rules governing optical transitions between Russell-Saunders states. Table I gives the values used in computing the fluorescence yield Y (photons emitted/laser pulse/sputtered Fe atom) following the theory of Wright *et al.*,⁴ which depends on the various laser and atomic parameters. For example, a similar calculation for the resonant $^2S_{1/2} \rightleftharpoons ^2P_{3/2}$ transition in Na, using a much longer pulse width ($1 \mu\text{sec}$), gave $Y = 41$, resulting from multiple excitations and de-excitations of each atom as it passes through the fluorescence sampling volume. For Fe^+ (Fe II), which could be detected via the $(3d^6 4s) a^6D_{9/2} \rightleftharpoons (3d^6 4p) z^6D_{9/2}^0$ resonance at $\lambda = 260.0 \text{ nm}$, $Y = 2.3$ for $t_L = 20 \text{ nsec}$, and $Y = 12.0$ for $t_L = 1 \mu\text{sec}$ (with values for I_L , $\Delta\lambda_L$, and t as in Table I).

Figure 3(b) shows the fluorescence signal (intensity vs time) averaged over 1024 laser shots for sputtering of the Fe foil. The one-shot SNR was $\sim 50/1$. Figure 3(c) shows a similar trace for LiNbO_3 , with the net gain increased a factor of 512, indicating an LIF signal down by a factor of 10^3 relative to pure Fe. The data in Fig. 3(c) have been corrected for the scattered light background by subtracting the signal obtained with the Ar^+ beam off from that with the beam on. No Fe signal was detected during sputtering of either the Si sample or the Al foil mask. In the absence of standard samples, a quantitative determination of the absolute Fe content is difficult. Independent secondary-ion mass spectrometry (SIMS) profiles of similar LiNbO_3 samples (R. J. Colton, NRL) indicate a surface-iron signal which is 30–50 times

greater than that of the bulk. The bulk-iron content (as determined by the supplier using spark-source mass spectrometry) is ~ 10 ppm. Hence the magnitude of the LiNbO_3 Fe LIF signal is indeed reasonable and is a factor of ~ 5 above the present noise level. The signal was also seen to decrease with prolonged sputtering.

The mechanism whereby zero-valent Fe atoms are removed during sputtering of an ionic host (LiNbO_3) requires brief comment. For clean metal surfaces, neutral species dominate the sputtering yield¹⁰; whereas, for oxidized surfaces, ejection of ions is enhanced. However, for oxides of polyvalent metal ions preferential removal of oxygen results in a partial reduction of surface metal ions. This is clearly observed in the Nb 3d core-level x-ray photoemission spectrum¹⁴ of LiNbO_3 . For the case of Fe_2O_3 , it has been recently reported¹⁵ that Ar^+ -ion bombardment yields a surface on which 52% of the iron is Fe^{2+} and 21% Fe^0 . Thus we suggest that the reduction of surface ions by the Ar^+ beam can lead to ejection of neutrals from the LiNbO_3 surface.

Even with the present detection limit, LIF shows promise as a method to detect iron near the LiNbO_3 surface. Near-surface iron is most significant since guided wave structures take the form of the thin surface films a few microns deep. The results in Fig. 3 indicate that the pure Fe LIF is $\sim 5 \times 10^3$ above the noise level. Hence the present detection limit for Fe in a clean metallic host (neglecting any matrix effects on the sputtering process) is estimated to be ~ 200 ppm. There are several obvious and rather minor improvements that will appreciably increase sensitivity. The most important is a better system of light baffles (including Brewster-angle entrance and exit windows), since the present scattered-light signal (Ar^+ beam off) is only a factor of ~ 2 smaller than the Ar^+ beam-on signal for LiNbO_3 . Subsequent work on standard samples will serve to quantify the detection limit.

We thank R. F. Greene for suggesting the possibility of these experiments. We are grateful to C. H. Bulmer for providing

the LiNbO_3 samples and for helpful discussion. We also thank R. J. Colton for helpful comments. Mark Hoffbauer is an NRL-NRC Resident Research Associate.

References

1. R. L. Holman and P. J. Cressman, *Opt. Eng.* **21**, 1025 (1982).
2. K. P. Selter and H.-J. Kunze, *Phys. Scr.* **25**, 929 (1982).
3. A. Elbern and P. Mioduszewski, *J. Vac. Sci. Technol.* **16**, 2090 (1979).
4. R. B. Wright, M. J. Pellin, and D. M. Gruen, *Surf. Sci.* **110**, 151 (1981).
5. D. M. Gruen, A. R. Krauss, M. J. Pellin, and R. B. Wright, in *Chemistry and Physics of Solid Surfaces*, Vol. 4, R. Vanselow and R. Howe, Eds. (Springer, Berlin, 1982), p. 107.
6. W. Husinsky, G. Betz, and I. Girgis, *Phys. Rev. Lett.* **50**, 1689 (1983).
7. F. Frenkel, J. Häger, W. Krieger, H. Walther, C. T. Campbell, G. Ertl, H. Kuipers, and J. Segner, *Phys. Rev. Lett.* **46**, 152 (1981).
8. P. J. Hargis and M. J. Kushner, *Appl. Phys. Lett.* **40**, 779 (1982).
9. L. D. Talley, W. A. Sanders, D. J. Bogan, and M. C. Lin, *J. Chem. Phys.* **75**, 3107 (1981).
10. H. Oechsner, W. Rühe, and E. Stumpe, *Surf. Sci.* **85**, 289 (1979).
11. S. A. Schwarz and C. R. Helms, *Surf. Sci.* **102**, 578 (1981).
12. C. E. Moore, "Atomic Energy Levels," *Natl. Bur. Stand. (U.S.)* Circ. 467 (1952).
13. J. Reader, C. H. Corliss, W. L. Wiese, and G. A. Martin, "Wave-lengths and Transition Probabilities for Atoms and Atomic Ions," *Natl. Stand. Ref. Data. Ser., Natl. Bur. Stand. (U.S.)* **68** (1980).
14. R. Courths, P. Steiner, H. Höchst, and S. Hüfner, *Appl. Phys.* **21**, 345 (1980).
15. R. L. Kurtz and V. E. Henrich, *Surf. Sci.* **129**, 345 (1983).